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13. ABSTRACT *(Maximum 200 words)*

Virtually all of the progress and accomplishments have been described in detail in previous annual progress reports. These will not be repeated here. Only those few new results initiated in the last few months of the grant will be listed. POSS Systems: In the annual report submitted in September, 2002, we showed mass spectra of the StyxEpyT8 system synthesized at Edwards AFB, where x + y =8, Sty stands for styrene and Ep for styrene with the vinyl group epoxidated. The pure Sty8T8 system had been discussed in previous reports and the work has recently been written up for publication. We showed preliminary arrival time distributions and averaged cross sections for Sty7EpT8 and Sty6Ep2T8 in the September, 2002, progress report. Since then we have also been able to obtain ATDs for the Sty5Ep3T8 species and have taken all 3 systems to 110 K to improve resolution. In each case we can resolve 3 isomers in the ATDs. Examples are given in Fig. 1 for Sty7EpT8 and Sty6Ep2T8. In Sty7EpT8 the isomers occur due to pairing of the non epoxided styryl capping groups (0 pairs, 1 pairs) while in Sty6Ep2T8 and Sty5Ep3T8 the isomers are due to different arrangements of the Ep capping groups on the T8 cage. The 3 possibilities for the Sty6Ep2T8 system were shown in the September, 2002 progress report. In Fig. 2 we show the 3 possibilities for the Sty5Ep3T8 system, the experimental cross sections and the cross sections from our theoretical modeling. Sty-Sty pairs are shown in blue. Clearly the agreement is excellent giving confidence in the results. It is interesting that Sty-Sty pairing is only observed in cases where there is no epoxide adjacent to the styryl capping agent.

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FINAL REPORT

Structures and Energetics of Clusters and Macromolecules

AFOSR Grant F49620-99-1-048

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I. Abstract/Status

Progress has been made on the objectives listed below. These have been described in substantial detail in the various annual Progress Reports and in the Renewal Proposal, recently funded as F49620-03-1-0046 with a start date of 01/01/03. Only a very brief summary will be given in Section III below.

II. Objectives

A. Characterization of the growth, structures, energetics and reactivity of metallic, semiconductor, composite and molecular clusters.

B. Determination of the conformations and energetics of synthetic and biopolymers.

C. Develop the instrumentation, theory and methodology to accomplish A and B above.

III. Progress and Accomplishments

Virtually all of the progress and accomplishments have been described in detail in previous annual progress reports. These will not be repeated here. Only those few new results initiated in the last few months of the grant will be listed.

A. POSS Systems

In the annual report submitted in September, 2002, we showed mass spectra of the $Sty_xEp_yT_8$ system synthesized at Edwards AFB, where x + y = 8, Sty stands for styrene and Ep for styrene with the vinyl group epoxidated. The pure Sty_8T_8 system had been discussed in previous reports and the work has recently been written up for publication.

We showed preliminary arrival time distributions and averaged cross sections for Sty_7EpT_8 and $Sty_6Ep_2T_8$ in the September, 2002, progress report. Since then we have also been able to obtain ATDs for the $Sty_5Ep_3T_8$ species and have taken all 3 systems to 110 K to improve resolution. In each case we can resolve 3 isomers in the ATDs. Examples are given in Fig. 1 for Sty_7EpT_8 and

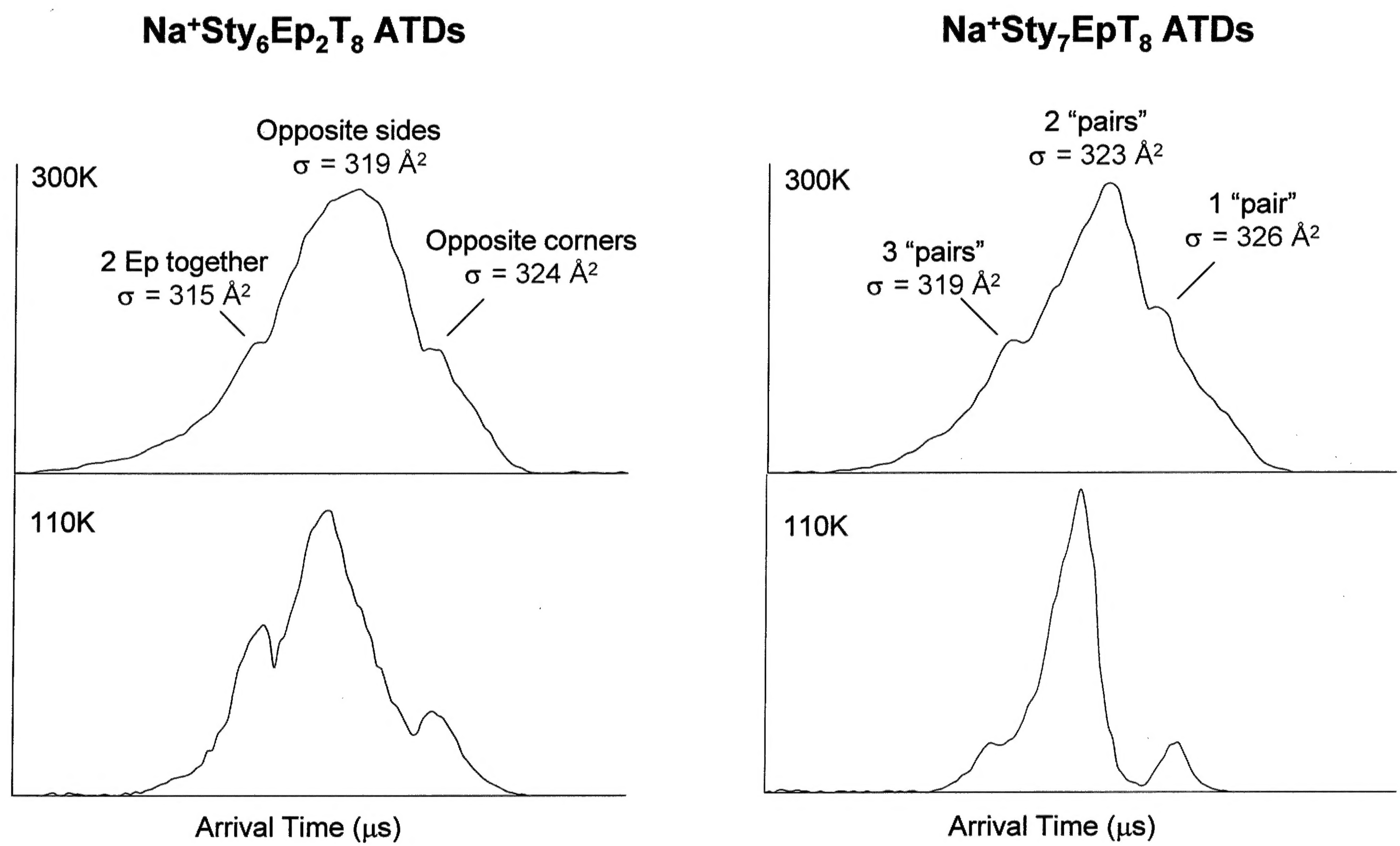
$Sty_6Ep_2T_8$. In Sty_7EpT_8 the isomers occur due to pairing of the non epoxided styryl capping groups (0 pairs, 1 pair, 2 pairs) while in $Sty_6Ep_2T_8$ and $Sty_5Ep_3T_8$ the isomers are due to different arrangements of the Ep capping groups on the T_8 cage. The 3 possibilities for the $Sty_6Ep_2T_8$ system were shown in the September, 2002 progress report. In Fig. 2 we show the 3 possibilities for the $Sty_5Ep_3T_8$ system, the experimental cross sections and the cross sections from our theoretical modeling. Sty-Sty pairs are shown in blue. Clearly the agreement is excellent giving confidence in the results. It is interesting that Sty-Sty pairing is only observed in cases where there is no epoxide adjacent to the styryl capping agent. The epoxide rotates the phenyl group such that it has a T-shape interaction with the phenyl group on the adjacent styryl. This is a robust result as pairing has a substantial effect on the cross section. Hence, with these quick, simple measurements (Mass Spectrum, ATDs) we are able to unambiguously determine how much of a particular species is formed in the synthesis (i.e. x, y in $Sty_xEp_yT_8$), the degree of pairing of styryl groups and the distribution of the epoxidized groups on the T_8 cage. In cases where structurally specific location(s) are desired, information such as this is essential. Similar information cannot be obtained by other structural methods (NMR, Xray) and the ion mobility method uses only nanomoles of material.

B. Electro-optical Materials

In earlier reports (September, 2001 and the renewal proposal) we discussed preliminary work on oligophenyl vinylenes. These materials have important electro-optical properties. Our earlier work focused on single chain oligomers of 5 and 6 repeat units. Recently we have begun work on four of these oligomers attached to a single tetrahedral carbon center. The idea is these "jack like" molecules will resist crystallization while retaining the optical properties of the isolated arms. The synthetic strategy was to make all four arms with trans only vinyl linkages (i.e. quasi linear) to maximize both the resistance to crystallization and the optical properties of each arm.

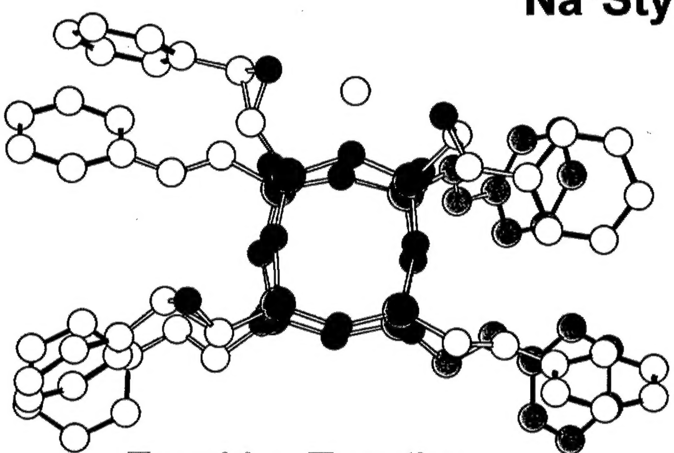
Our work in these systems is still in progress. However, we can say unambiguously that the "all trans" species is a very minor player (<1%) and the vast majority have one or more Cis defects in the vinyl group closest to the tetrahedral carbon leading to arm-arm interactions. The modeling for these systems is very complex but nearly complete. Initial indications are we can unambiguously identify all features observed in the very complex ATDs we measure. These data and their analysis will provide invaluable information to the synthetic group (led by Prof. Gui Bazan at UCSB) in designing new methods of synthesis.

Figure 1



$Na^+Sty_6Ep_2T_8$ ATDs
Opposite sides
σ = 319 Å²
2 Ep together
σ = 315 Å²
Opposite corners
σ = 324 Å²
300K
110K
Arrival Time (µs)
$Na^+Sty_7EpT_8$ ATDs
2 "pairs"
σ = 323 Å²
3 "pairs"
σ = 319 Å²
1 "pair"
σ = 326 Å²
300K
110K
Arrival Time (µs)

Figure 2
$Na^+Sty_5Ep_3T_8$ Theoretical Structures

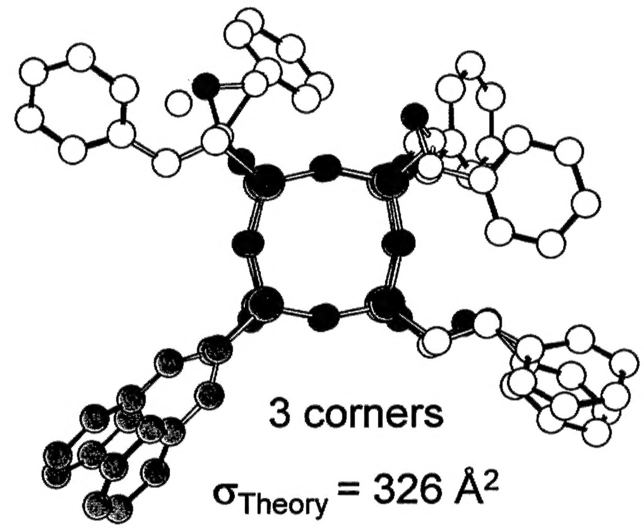


Epoxides Together

$\sigma_{Theory} = 314$ Å^2

$\sigma_{EXPT} = 314$ Å^2

Abundance = ~17%

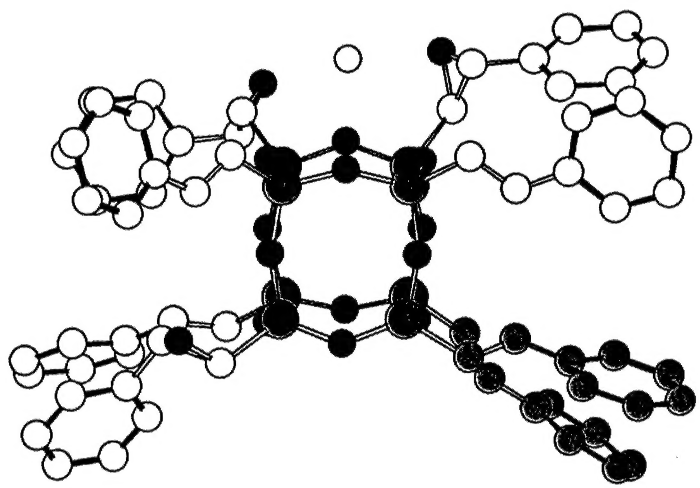


3 corners

$\sigma_{Theory} = 326$ Å^2

$\sigma_{EXPT} = 327$ Å^2

Abundance = ~17%



2 together and 1 on the opposite side

$\sigma_{Theory} = 319$ Å^2

$\sigma_{EXPT} = 319$ Å^2

Abundance = ~66%

IV. Papers Published or In Press

1. Cluster Assisted Thermal Energy Activation of the H-H Sigma Bond in H_2 by Ground State $B^+(^1S_\Phi)$ Ions: Overcoming a 77 kcal/mol Barrier, Paul R. Kemper, John E. Bushnell, Patrick Weis and Michael T. Bowers, *J. Am. Chem. Soc.*, **120**, 7577-7584 (1998).

2. Gas Phase Conformations of Biological Molecules: The Hydrogen/Deuterium Exchange Mechanism, Thomas Wyttenbach and Michael T. Bowers, *J. Am. Soc. Mass Spectrometry*, **10**, 9 (1999).

3. Binding Between Ground State Aluminum Ions and Small Molecules: $Al^+(H_2/CH_4/C_2H_2/C_2H_4/C_2H_6)_n$; Can Al^+ Insert into H_2?, Paul R. Kemper, John E. Bushnell, Michael T. Bowers and Greg I. Gellene, *J. Phys. Chem.* A, Sidney Benson Honor Issue, **102**, 8590 (1998).

4. Gas Phase Conformations of Synthetic Polymers: Poly (Methyl Methacrolate) (PMMA) Oligomers Cationized by Sodium Ions, Jennifer Gidden, Anthony T. Jackson, James H. Scrivens and Michael T. Bowers, *Int. J. Mass Spectrometry*, Brian Green Honor Issue, **188**, 121 (1999).

5. Folding Energetics and Dynamics of Macromolecules in the Gas Phase: Alkali Ion Cationized Poly (Ethylene Terephthalate) (PET) Oligomers, Jennifer Gidden, Thomas Wyttenbach, Joseph J. Batka, Patrick Weis, Anthony T. Jackson, James H. Scrivens and M.T. Bowers, *J. Am. Chem. Soc.*, **121**, 1421 (1999).

6. Energetics and Structures of Gas Phase Ions: Macromolecules, Clusters and Ligated Transition Metals, Michael T. Bowers, Paul R. Kemper, Petra van Koppen, Thomas Wyttenbach, Catherine J. Carpenter, Patrick Weis and Jennifer Gidden, NATO ASI, "Energetics of Stable Molecules and Reactive Intermediates", Castelo Branco, Portugal, July, 1998, pp. 235-258.

7. Poly (ethylene terphthalate) (PET) Oligomers Cationized by Alkali Ions: Structures, Energetics and Their Effects on Mass Spectra and the MALDI Process, Jennifer Gidden, Thomas Wyttenbach, Joseph J. Batka, Patrick Weis, Anthony T. Jackson, James H. Scrivens, and Michael T. Bowers, *J. Am. Soc. Mass Spectrom*, R. Squires Beimann Medal Special Issue **10**, 883 (1999).

8. Host/Guest Conformations of Biological Systems: Valinomycin/Alkali Ions, Thomas Wyttenbach, Joseph J. Batka Jr., Jennifer Gidden and Michael T. Bowers, *Int. J. Mass Spectrometry*, Special Issue on Host/Guest Chemistry, **193**, 144 (1999).

9. On the Question of Salt Bridges of Cationized Amino Acids in the Gas Phase: Glycine and Arginine, Thomas Wyttenbach, Matthias Witt and Michael T. Bowers, *Int. J. Mass Spectrometry*, Ion Proc., Ben S. Freiser Memorial Issue, **182/183**, 243-252 (1999).

10. Conformations of Biopolymers in the Gas Phase: a New Mass Spectrometric Method, A.C. Gill, K.R. Jennings, T. Wyttenbach and M.T. Bowers, *Int. J. Mass Spectrom*, Robert Squires Memorial Issue **195/196**, 685 (2000).

11. Gas Phase Conformations of Synthetic Polymers: Poly (ethylene glycol), Poly (propylene glycol), and poly (tetramethylene glycol), J. Gidden, T. Wyttenbach, J.H. Scrivens and M.T. Bowers, *J. Am. Chem. Soc.* **122**, 4692 (2000).

12. On the Stability of Amino Acid Zwitterions in the Gas Phase: The Influence of Derivatization, Proton Affinity and Alkali Ion Addition, T. Wyttenbach, M. Witt and M.T. Bowers, *J. Am. Chem. Soc.* **122**, 3458 (2000).

13. Gas Phase Conformations and Folding Energetics of Oligonucleotides: dTG^- and dGT^-, J. Gidden, J.E. Bushnell and M.T. Bowers, *J. Am. Chem. Soc.*, **123**, 5610 (2001).

14. Gas-Phase Conformations of Cationized Poly(styrene) Oligomers, J. Gidden, A.T. Jackson, J.H. Scrivens, M.T. Bowers, *J. Am. Soc. Mass Spectrom*, **13**, 499 (2002.

15. Gas-Phase Conformational and Energetic Properties of Deprotonated Dinucleotides, J. Gidden and M.T. Bowers, *European J. Phys. D.*, **20**, 409 (2002).

16. Application of Ion Mobility to the Gas-Phase Conformational Analysis of Polyhedral Oligomeric silsesquioxanes (POSS), J. Gidden, P.R. Kemper, E. Shammel, D.P. Fee, S. Anderson, M.T. Bowers, *Int. J. Mass Spectrom*, **222**, 63 (2002).

17. Conformation and Luminescence of Isolated Molecular Semiconductor Molecules, M.A. Summers, P.R. Kemper, J.E. Bushnell, M.R. Robinson, G.C. Bazan, M.T. Bowers, S.K. Buratto, *J. Am. Chem. Soc.* (submitted).

18. 3-Dimensional Structural Characterization of Cationized Polyhedral Oligomeric Silsesquioxanes (POSS) with Styryl and Phenethyl Capping Agents, E. Shammel Baker, J. Gidden, D.P. Fee, P.R. Kemper, S. Anderson, M.T. Bowers, *Int. J. Mass Spectrom* (in press).

19. Gas-Phase Conformations of Deprotonated Trinucleotides ($dGTT^-$, $dTGT^-$ and $dTTG^-$): The Question of Zwitter Ion Formation, J. Gidden, M.T. Bowers, *J. Am. Soc. Mass Spectrom* (in press).

V. Personnel Supported

A. Senior

Dr. Paul Kemper
Dr. Thomas Wyttenbach
Dr. Joe Batka
Dr. Patrick Weis
Dr. Matthias Witt
Dr. Stan Anderson

B. Junior

Ms. Jennifer Gidden
Mr. Jason Souza
Mr. Manuel Manard
Ms. Erin Shammel
Mr. David Fee

VI. Papers Presented

A. Invited Lectures at Meetings

1. Tutorial Lecture on "The Anatomy of a Collision and its Consequences", 47th Meeting of the American Society of Mass Spectrometry, Dallas, TX, June 1999.

2. Symposium on Mass Spectrometry, ACS Regional Meeting, Ontario, CA, October 1999.

3. Cluster Cooling Workshop, Jerusalem, April 2000.

4. Keynote Lecture, Triennial International Conference on Mass Spectrometry, Barcelona, Spain, August 2000.

5. Air Force Contractors Meeting, Newport Beach, May, 2001.

6. Keynote Lecture, Symposium on Ion Mobility, American Society for Mass Spectrometry, Chicago, IL, May, 2001.

7. Invited Speaker, Symposium on Three-Dimensional Silicon-Oxygen Cages: Materials for the 21st Century, ACS Meeting, Chicago, IL, Aug. 2001.

8. Invited Lecture, Symposium on Mass Spectrometry, FACSS Meeting, Detroit, MI, Oct. 2001.

9. Invited Speaker, Gordon Conference on Molecular and Ionic Clusters, Ventura, CA, Jan. 2002.

10. Invited Speaker, Symposium on Biological Molecules in the Gas Phase, APS Meeting, Indianapolis, IN, March 2002.

11. Invited Speaker, Award Symposium in Analytical Chemistry, ACS Meeting, Orlando, FL, April 2002.

12. Keynote Lecturer, Symposium on Zwitter Ions, Am. Soc. Mass Spectrom Meeting, Orlando, FL, June, 2002.

13. Invited Speaker, Symposium on Copolymers, ASMS Meeting, Orlando, FL, June 2002.

14. Invited Speaker, Symposium on Biological Molecules in the Gas Phase, American Chemical Society Meeting, Boston, MA, August, 2002.

A. Contributed Papers

1. Presented four papers, West Coast Ion Chemistry Conference, Lake Arrowhead, CA, January 1999.

2. Presented one paper, Industrial Polymers Symposium, 47th Annual ASMS Conference, Dallas, TX, June 1999.

3. Presented four papers, West Coast Ion Chemistry Conference, Lake Arrowhead, CA, January 2000.

4. Presented poster, AFOSR Contractors Meeting, Boston, MA, June 2000.

5. Presented 4 papers, West Coast Ion Chemistry Conference, Lake Arrowhead, CA, January 2001.

6. Presented 4 papers, Ion Chemistry Conference, Lake Arrowhead, CA, Jan. 2002.

C. Invited Seminars

1. Cal Tech, April 1999.

2. Westmont College, April 1999.

3. University of Metz, Metz, France, April 2000.

4. Hebrew University, Jerusalem, Israel, April 2000.

5. Welch Foundation Lecturer in Texas: Visits and seminars to Tarleton State University, St. Edwards University and Rice University, November 2000.

6. Frontiers in Chemistry Lecturer, Wayne St. Univ., Detroit, MI, April 2002.

7. University of Southern California, April, 2002.

8. University of Texas at Arlington, October, 2002.

9. Frontiers in Chemistry Lecturer (3 lectures) Texas A&M University, November, 2002.

VII. Honors and Awards

Continuing/Prior

1. Honoree of a Special Issue of the International Journal of Mass Spectrometry. There were 84 papers, comprising all of Vols 185, 186, and 187 and 1017 journal pages (June 1999).

2. Fellow American Physical Society, (elected 1987)

3. Fellow American Association of the Advancement of Science (elected 1994)

4. Fellow, John Simon Guggenheim Foundation (1995 Calendar Year)

5. Nobel Laureate Signature Award, American Chemical Society (1989)

6. Faculty Research Lecturer, University of California at Santa Barbara (1994)

7. Frank H. Field and Joe L. Franklin Award for Outstanding Achievement in Mass Spectrometry, American Chemical Society (1996)

8. Thomson Gold Medal, International Mass Spectrometry Society (1997)

VIII. Transitions

1. Our work on Industrial Polymers continues to attract interest in that community. We have recently received a major gift from ICI in support of this program and are in discussion with people at DuPont.

2. I have recently been asked to be on the Scientific Advisory Board for a new biotechnology start up company, EpigenX. My expertise in MALDI of macromolecules gained with the support of AFOSR was the principal reason for the appointment.

IX. New Discoveries, Innovations or Patent Disclosures

None